OFFICIAL DOCUMENT

Albuquerque Bernalillo County

Water Utility Department

WATER RECLAMATION DIVISION
4201 2ND STREET SW, ALBUQUERQUE, NEW MEXICO 87105

WATER QUALITY LABORATORY
STANDARD OPERATING PROCEDURE APPROVAL FORM

WQL SOP **SOP 209**
Renumbered 5/12/2010

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MODIFICATIONS AND REASONS FOR REVISION

***New WQL Management Staff**
***New SOP Numbering System**
***New QA/QC Filing System**
***Revised Quality Control Section**

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Out of Service By: _____ Date: ___/___/___

Reason:

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STANDARD OPERATING PROCEDURE

SOP 208

TOTAL HARDNESS

SCOPE AND APPLICATION: This method is applicable to drinking, surface and saline waters, domestic and industrial wastes. This method is applicable for all concentration ranges.

APPLICABLE METHOD REFERENCES: 19th ed. of Standard Methods, 2340 C.

DISPOSAL OF SAMPLES: Dispose of samples at an acid sink.

Effective Date 5/23/06

TOTAL HARDNESS

1.0 GENERAL DISCUSSION

1.1 Principle: Ethylenediaminetetraacetic acid and its sodium salts(EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ∀ 0.1, the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexes, and when all of the magnesium and calcium has been complexes the solution turns from wine red to blue, marking the end point of the titration. Magnesium ion must be present to yield a satisfactory end point. To insure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction.

The sharpness of the end point increases with increasing pH. However, the pH cannot be increased indefinitely because of the danger of precipitating calcium carbonate or magnesium hydroxide, and because the dye changes color at high pH values. A limit of 5 minutes is set for the duration of the titration to minimize the tendency toward calcium carbonate precipitation.

1.2 Interferences: Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Reduce interference by adding inhibitors before titration. MgCDTA, selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for more toxic inhibitors, It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness. With heavy metal or polyphosphate concentrations below those indicated in the Table use Inhibitor I or II.

Suspended or colloidal organic matter also may interfere with the end point. Eliminate this interference by evaporating the sample to dryness on a steam bath and heating in a muffle furnace at 550EC until the organic matter is completely oxidized. Dissolve the residue in 20mL 1N HCL, neutralize to pH 7 with 1N NaOH, and make up to 50 mL with distilled water; cool to room temperature and continue according to the general procedure.

TABLE: Maximum Interference Concentration mg/L

Interfering Substance	Inhibitor I	Inhibitor II
Aluminum	20	20
Barium	H	H
Cadmium	H	20
Cobalt	>20	0.3
Copper	>30	20
Iron	>30	5
Manganese	H	1
Lead	H	20
Nickel	>20	0.3
Strontium	H	H
Zinc	H	200

Interfering Substance	Inhibitor I	Inhibitor II
Polyphosphate		10

1.3 Safety Considerations: The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Wear protective gloves, laboratory coat and eye protection. Dispose of all samples and reagents in an acid sink. Reagents used are potentially caustic or corrosive, avoid ingestion or inhalation and contact with the skin. For specific hazards consult the MSDS sheet, located in the laboratory office for compounds listed in section 3.0.

1.4 Sample Preservation & Storage: Use polyethylene or glass bottles for sample collection and store at a low temperature. Fill bottles completely and cap tightly. Samples are preserved by acidification of the sample to a pH of <2 with nitric acid. Once preserved, samples may be stored up to six months.

1.5 Sample Preparation: Allow samples to come to room temperature ~25NC.

1.6 Method Performance Criteria: The reference method Std. Methods 19th ed. cites: A synthetic sample analyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

2.0 APPARATUS & EQUIPMENT: 100 mL beakers, 50 mL buret, magnetic stirrer, stir bar.

3.0 REAGENTS & SUPPLIES:

3.1 Buffer solution: Dissolve 16.9g ammonium chloride in 143 mL concentrated ammonium hydroxide. Add 1.25g magnesium salt of EDTA and dilute to 250 mL with reagent

3.2 Inhibitor I: Adjust acid samples to pH 6 or higher with buffer or 0.1N NaOH. Add 250mg sodium cyanide (NaCN) in powder form. Add sufficient buffer to adjust to pH 10.0 ∀ 0.1. **Caution: NaCN is extremely poisonous. Take extra precautions in its use. See SOP AC-010 Total Cyanide for procedure for the disposal of sample containing cyanide.**

3.3 Inhibitor II: Dissolve 5.0g sodium sulfide nonahydrate in 100mL reagent water. Exclude air with a tightly fitting rubber stopper. This inhibitor deteriorates through air oxidation. It produces a sulfide precipitate that obscures the end point when appreciable concentrations of heavy metals are present. Use 1 mL in Mg-CDTA.

3.4 Mg-CDTA: Magnesium salt of 1, 2-cyclohexanediamine-tetraacetic acid. Add 250 mg per 100 mL sample and dissolve completely before adding buffer solution. Use this complexing agent to avoid using toxic or odorous inhibitors when interfering substances are present in concentrations that affect the end point but will not contribute significantly to the hardness value.

3.5 Calmagite: 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid. This is stable in aqueous solution and produces the same color change as Eriochrome Black T, with a sharper end point. Dissolve 0.10g Calmagite in 100 mL reagent water. Use 1 mL per 50 mL solution to be titrated. Adjust volume if necessary. **Alternatively**, dry powder form may be used directly without hydration. Care must be taken to avoid excess indicator use when using the

powder form.

3.6 Standard EDTA titrant, 0.01M: Weigh 3.723g disodium ethylenediaminetetraacetate dihydrate also called (ethylenedinitrilo)tetra acetic acid disodium salt (EDTA), dissolve in reagent water, and dilute to 1000 mL. Standardize against standard calcium solution.

3.7 Standard Calcium Solution: Weigh 1.000g anhydrous calcium carbonate powder into a 500 mL Erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time, 1 + 1 HCL until $CaCO_3$. Has dissolved. Add 200 mL reagent water and boil for a few minutes to expel Carbon dioxide. Cool, add a few drops of methyl re indicator and adjust to the intermediate orange color by adding 3N ammonium hydroxide or 1 + 1 HCl, as required. Transfer quantitatively and dilute to 1000 mL with reagent water; 1mL = 1.00 mg $CaCO_3$.

Calculation:

mg $CaCO_3$ equivalent to 1.00mL EDTA titrant = $\frac{A}{B}$

where:
A = mL EDTA titrant, B = mL Calcium standard solution (0.01M).

3.8 Sodium hydroxide: NaOH, 0.1N.

4.0 QUALITY CONTROL PROCEDURE:

4.1 Laboratory Reagent Blank (LRB) is an aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. When the LRB value is > 1 mg/L, a fresh aliquot of the sample/s must be prepared and analyzed again for the affected analyte after the source of contamination has been corrected and acceptable LRB values have been obtained. If the affected sample are beyond their holding time or lack adequate volume to retest, these samples will not be reanalyzed. The results of the affected samples will be corrected by subtracting out the measured level of contamination and reporting the difference. The corrected samples will require text to qualify the data. The text should state the sample has been corrected due to a LRB greater than 1 mg/L.

4.2 Laboratory Control Sample (LCS) is an aliquot of reagent water or other blank matrices to which known quantities of method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The laboratory must analyze at least one LCS and one LCSD with each batch of samples. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved, any corrective action taken must be documented in the bound work sheet book concomitant with the analysis data. The laboratory must use LCS analyses data to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data become available, usually a minimum of 20-30 analyses, optional control limits can be developed from the percent mean recovery (X) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = X + 3S

LOWER CONTROL LIMIT = X - 3S

After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LCS. These data must be kept on file and be available for review. If the LCS is not within its control limits, then the affected samples must have text to qualify the data. The text should state the percent recovery achieved for the LFB.

Calculation of percent recovery for an LCS:

$$R = \frac{LCS - LRB}{s} \times 100$$

where: R = Percent recovery
LCS = Laboratory fortified blank.
LRB = Laboratory reagent blank.
s = Concentration equivalent of analyte added to fortify the LRB solution

4.3 Laboratory Control Sample Duplicate (LCSD) is prepped exactly like the LCS and measures precision of the methodology.

4.4 Quality Control Calculations:

To calculate a % Difference: $\frac{2(\text{Sample Result} - \text{Sample Result}')}{\text{Sample Result} + \text{Sample Result}'} \times 100$

To calculate a % Recovery: $\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{\text{Final Concentration of spike added*}} \times 100$

* Use the dilution formula to compute the final concentration of spike added ie. $V_1 \times C_1 = V_2 \times C_2$. The volume of spike solution added should not exceed 1-2% of the final volume.

where: C_1 = Concentration of spike solution
V_1 = Volume of spike solution added to sample
C_2 = **Final Concentration of spike added**
V_2 = Volume of sample

4.5 Control Charts- All quality control data will be entered in the lab share drive by analysts performing this test. Quality assurance reviews are performed weekly, for complete details of control chart performance evaluations see QA SOP-005.

5.0 PROCEDURE:

5.1 Titration of Samples: Allow samples to reach near room temperature. In general select sample volumes that requires less than 15mL EDTA titrant and complete titration within 5 minutes from time of buffer addition. Dilute 25 mL sample or other appropriately selected sample volume to a final volume of 50 mL with reagent water in a clean 100 mL beaker. Add 1-2 mL buffer solution. Usually 1mL will be sufficient to give a pH of 10.0 to 10.1. The absence of a sharp end-point color change in the titration usually means that an inhibitor must be added at this point or that the indicator has deteriorated. Add 1-2 drops indicator solution or an appropriate amount of dry-powder (calgamite). Add standard EDTA titrant slowly, with continuous stirring, until the last reddish ting disappears. . Add the last few drops at 3-5 second intervals. At the end point the solution normally is blue.

5.2 Low Hardness Samples: For ion-exchanger effluent or other softened water and for natural waters of low hardness (less 5 mg/L), take a larger sample, 100-1000 mL, for titration and add proportionately larger amounts of buffer, inhibitor, and indicator. Add standard EDTA titrant slowly from a micro buret and run a blank, using reagent water of the same volume as the sample, to which identical amounts of buffer, inhibitor, and indicator have been added. Subtract volume of EDTA used for blank from volume of EDTA used for sample.

6.0 CALCULATION:

Hardness (EDTA) as mg $CaCO_3/L = \frac{A \times B \times 1000}{C}$

where:

A = mL EDTA titrant for sample,
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant and,
C = mL sample.

7.0 REPORTING: All measurements and results will be reported to three significant figure and recorded in the bound work sheet book for Hardness. The determined results for each sample tested and will be entered on the electronic data system, SQLLMS. All samples requiring qualification will be text at the sample level in SQLLMS. All analyses requiring corrective actions will have the documentation of the corrective action in the bound work sheet book, concomitant with the sample results, calibration and QC results. QC results will be entered in Excel an up to dated control chart produced.